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ITOH ET AL.

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Filed: August 14, 2006

Examiner: Y. Zhang

For: LASER DEVICE AND LASING METHOD

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DECLARATION UNDER 37 CFR § 1.132

Tadashi Itoh and Masaaki Ashida declare the following:

1. We are the original, first and joint inventors of the subject matter which is claimed in this application.

2. On information and belief, we understand that the Examiner rejected claims 1-4 and 6-9 under 35 U.S.C. 102(a) because he concluded they are anticipated by Kagotani et al. ("Laser Emission by Two-photon Resonant Excitation of Biexciton State in CuCl Quantum Dots", Research Institute of Electrical Communication, Tohoku University, vol. 14, pp. 247-250, 2003) (IDS filed on 08/14/06).

3. The reference, Kagotani et al. (2003) which was relied upon by the Examiner in his Section 102(a) rejection, has a publication date of December 5, 2003.

4. Tadashi Itoh, Masaaki Ashida and Yuji Kagotani, Goro Ohata, Kensuke Miyajima, Shingo Saito, Keiichi Edamatsu are authors of the reference Kagotani et al. (2003).

5. Yuji Kagotani, Goro Ohata, Kensuke Miyajima, Shingo Saito, Keiichi Edamatsu is not a joint inventor of the invention claimed in this application.

6. This application is the U.S. national phase of International Application PCT/JP2004/011536 filed on August 11, 2004.

7. On information and belief, the international filing date of August 11, 2004 of the claims pending in this application is less than one year after the publication of the reference Kagotani et al. (2003).

8. The undersigned declare that all statements made herein of their personal knowledge are true and that all statements were made with the knowledge that any willful false statements are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that willful false statements may jeopardize the validity of this patent application or any patent issuing thereon.

April 6, 2011
Date

Tadashi Itoh
Tadashi Itoh

April 6, 2011
Date

Masaaki Ashida
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Ultrafast emission under two-photon excitation of biexcitons in CuCl quantum dots

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Time-resolved photoluminescence spectra of biexcitons confined in CuCl quantum dots have been measured by means of an optical Kerr-gate method. When the biexcitons are generated by resonant two-photon excitation, a new ultrashort photoluminescence is observed. This result indicates that the resonant two-photon excitation of the biexcitons induces a new transition process with a large optical nonlinearity which is characteristic for the direct generation.

1 Introduction

Optical properties of semiconductor quantum dots (QDs) have received much attention because of the discrete electronic levels and large optical nonlinearities according to three-dimensional confinement in this system [1]. The optical nonlinear response in the QDs is induced by the large correlation between the carriers. Therefore, it is very important to study dynamics of the excitonic complexes to find proper quantum structures for the optical devices, e.g. quantum dot lasers. The biexciton (bound two exciton state) is one of the excitonic complexes possessing a large optical nonlinearity, and this property is affected by correlation between excitons in the QDs.

CuCl QDs show typical properties of the weak confinement regime because of the small exciton Bohr radius ($a_B = 0.7$ nm) [2]. The biexciton properties in CuCl QDs has been investigated very much, for example, quantization of the center-of-mass motion [3], the larger binding energy [3, 4] compared to the bulk crystal (32 meV for Γ_5 excitons [5]), the biexciton formation and relaxation dynamics [6–8] and the laser emission [9]. In the bulk crystal, the resonant two-photon absorption of the biexciton occurs efficiently, which is called a giant two-photon absorption [5, 10]. For the CuCl QDs, on the other hand, the two-photon absorption processes have been confirmed by photoluminescence (PL) excitation spectra of the biexciton. The biexciton PL intensity was decreased with circularly polarized excitation compared to the linearly one, which agree with the polarization selection rule for the lowest biexciton state with the total angular momentum $J = 0$ [11]. Furthermore, under two-photon excitation, a highly efficient and subsequently stable laser emission from the biexciton state was observed [12, 13]. Figure 1 shows the PL spectra (solid lines) under two-photon excitation with several excitation intensities, together with the absorption spectrum (dashed line). When the excitation intensity was lower than the threshold for lasing, the M and BM bands which were assigned to the PL from the free (intrinsic) and bound (extrinsic) biexciton states, respectively, and the I_1 line due to an exciton bound to a neutral acceptor were observed [6, 7]. With increasing the excitation intensity, the laser emission emerged and increased superlinearly. It

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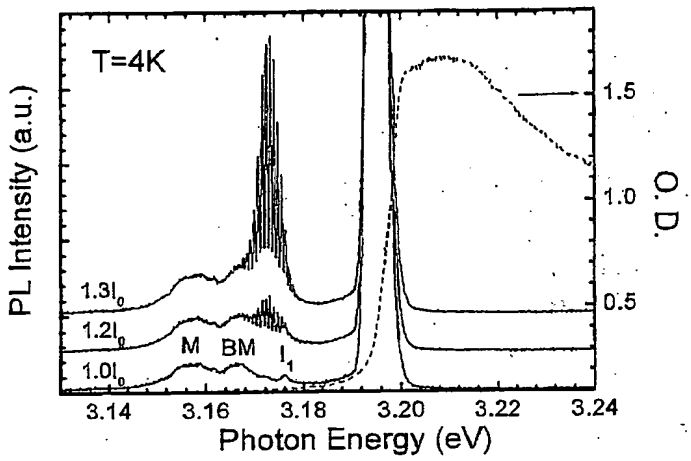

Fig. 1 PL spectra under two-photon excitation of the biexciton in CuCl QDs at 4 K with the excitation intensities of 1.0, 1.2 and $1.3I_0$, where I_0 was 0.12 mJ/cm^2. The excitation light was obtained by using an optical parametric amplifier (pulse duration of ~2 ps, spectral width of ~3 meV and repetition rate of 1 kHz). The excitation photon energy was tuned to 3.195 eV. Denotation of M, BM and I_1 are explained in text. The dashed line shows the absorption spectrum.

was confirmed that the laser emission occurs through the biexciton state because it disappeared with circularly polarized excitation light. However, the emitted photon energy was different from that of the M and BM bands. Consequently, the transition process from the biexciton to the exciton state originating the lasing is still ambiguous. In addition, this transition process should emerge at the ultrafast stage because the laser emission occurs in spite of the low reflectivity (R = ~5%) of the optical cavity consisting of the cleaved NaCl surfaces. Therefore, time-resolved PL measurements are necessary to clarify the mechanism of the laser emission.

In this paper, we report the ultrafast biexciton dynamics in CuCl QDs by means of time-resolved PL spectroscopy with the use of an optical Kerr-gate method. We observed a new PL band, which emerges at the ultrafast stage only under two-photon excitation. From this result, the transition process for the new PL band will be discussed, where the biexciton states for the M and BM bands should be reconsidered.

2 Experimental

CuCl QDs embedded in a NaCl matrix were fabricated by a transverse Bridgman method [14]. The nominal dot concentration was ~1 mol% and the average dot radius was ~7 nm. The sample was cleaved with a thickness of less than 500 μm. The Kerr gate spectroscopy was performed by using the pulse laser system based on a regenerative amplifier (pulse width of 220 fs, wavelength of 800 nm, repetition rate of 1 kHz). The laser light from the regenerative amplifier was separated into two for the Kerr gate light and the pump light for an optical parametric amplifier (OPA), respectively. The excitation light was obtained from a fourth harmonic generation by using two β-BBO crystals for a signal beam from the OPA. The spectral width of the excitation light was ~12 meV. Toluene in a quartz cell was used as the Kerr medium. The time resolution of the measurement system was ~1.2 ps. The excitation light was irradiated on the sample in a stripe-shape with a length of 800 μm through a cylindrical lens. The PL from an edge of the sample was collected and detected by using a spectrometer equipped with a charge-coupled device. The sample was cooled down to 15 K in a He-flow cryostat.

3 Results and discussion

The time-integrated PL spectra and the time-resolved PL images under resonant excitation of the exciton (excitation energy of 3.209 eV) and resonant two-photon excitation of the biexciton (3.192 eV) are

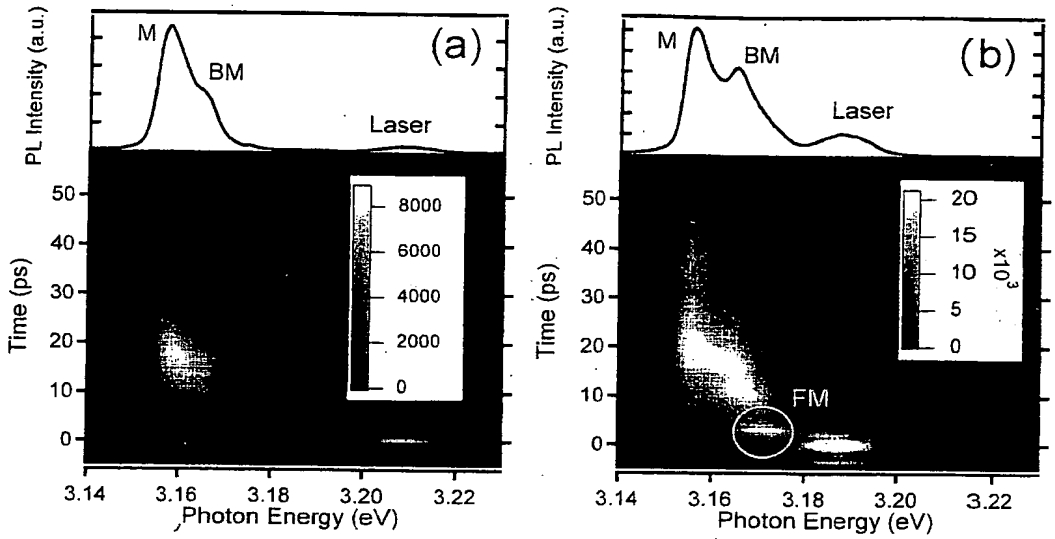

Fig. 2 Time-integrated PL spectra (upper) and time-resolved PL images (lower) under resonant excitation of the excitons (a), and under two-photon resonant excitation of the biexcitons (b), respectively. The spectral width of the excitation laser was ~12 meV. The PL intensities in the time-integrated spectra are nomalized.

shown in Fig. 2(a) and (b), respectively. The excitation intensities were 2.3 and 3.5 mJ/cm^2, respectively. In the case of resonant excitation of the excitons, the M band was dominant. The PL of the free or bound exciton states was not observed because of the effective reabsorption process. The PL intensity of the M band reaches its maximum at a delay time of 20 ps, and decays rapidly with a time constant of 11 ps. Under two-photon excitation, on the other hand, the M and BM bands were observed separately. The delay times of their maxima are 20 and 11 ps, respectively, and the decay curves are not exponential. In addition, a new PL band at 3.173 eV emerged before the rise of the BM band. Hereafter, we call this new band FM band. The FM band emerges only under two-photon excitation with strong excitation intensity. Figure 3 shows the time-resolved PL spectra at the delay times in steps of 3 ps. The FM band was observed clearly at a delay time of 3 ps. Since the FM band disappeared under circularly polarized excitation light, it is concluded that it originates from the biexciton state. Therefore, we have to consider a new transition process from the biexciton to exciton states, which has not been discussed yet. In the following, we will discuss two points: the delay and decay times of the M and BM bands, and the origin of the FM band.

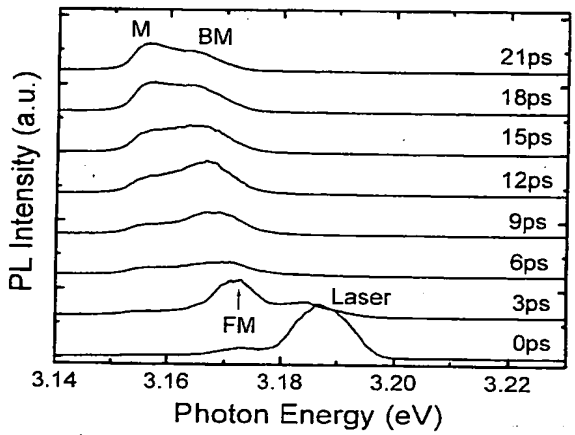

Fig. 3 Time-resolved PL spectra under the resonant two-photon excitation of the biexciton at several delay times shown in their right hand side. The arrow indicates the new PL band denoted by FM discussed in the text.

The decay times of the M and BM bands were reported previously as 125 and 70 ps, respectively [6]. It is suggested that the decay times in this measurement are faster due to the stimulated emission which can easily becomes dominant towards the longer excitation length. On the other hand, the delay times of the maxima for the M and BM bands are longer than previously reported values which are less than 10 ps under band-to-band excitation [7]. The longer delay time is not caused by the propagation of the emission because the excitation length of 800 μm corresponds to the delay time of ~4 ps by considering the refractive index of the NaCl matrix ($n = \sim 1.5$). It is thought that the delay time with respect to the maximum intensity should not be beyond the 4 ps, although the stimulated emission may change the timeprofile. Therefore, it is suggested that the relaxation times to the initial biexcitonic states for the M and BM bands depend on the excitation conditions. In the case of resonant excitation of the exciton, the restricted interaction with the phonons due to the quantized energy levels of the excitons is considered to make the generation time of the biexciton slower compared to the case of the band-to-band excitation, where the biexcitons are generated by two electrons and holes with large wave-vectors. On the other hand, in the case of two-photon excitation, it is expected that the delay times are very short because the biexcitons are generated directly. The unexpectedly long delay time for the M band indicates that the initial state for the M band can not be free biexciton states which are resonantly excited.

Next, the origin of the FM band is discussed. We assumed two possibilities for the origin of the FM band. First, the origins of the ordinal M band are reconsidered. Until now, the origin of the M band has been suggested to be due to free biexcitons because it becomes dominant with increasing the temperature. However, there remains the unsolved question that the PL energy of the M band does not agree with the induced absorption energy from the exciton to biexciton states [3, 4]. Therefore, assuming that the M band is due to the radiative relaxation not from the free biexciton but from a biexciton trapped to a shallow impurity, we can say that, in reality, the FM band originates from the free biexciton state. The long delay time of the M band supports this assumption. The next assumption is that the new transition might be related to the triplet state. In the QDs, the exciton triplet state ($J_{ex} = 0$) is sometimes mixed with the singlet state ($J_{ex} = 1$), so that the optical transition becomes partially allowed. In the case of the biexciton, it is reasonable to suggest the transition from the biexciton state with $J = 1$, which is partially mixed with the lowest state with $J = 0$, to the triplet exciton state. These assumptions remain to be proved.

On the other hand, the FM band might be interpreted differently. The ultrashort time profile of the PL strongly suggests the Dicke's superradiance which originates from the coherent coupling of radiative dipoles over many excited QDs through the electromagnetic interaction [15]. In the initial stage, the resonant two-photon excitation of the biexciton provides the completely inverted population between the biexciton and exciton states, which easily realizes the condition of the occurrence of the superradiance. We will report this phenomenon elsewhere.

Finally, we discuss the possibility that the FM band might be the origin of the laser emission. The photon energy of the laser emission in Fig. 1 almost coincides with that of the FM band in Fig. 3. Therefore, it is strongly suggested that the laser emission originates from the FM band under the two-photon excitation. In the previous report on the laser emission, where the excitation laser has a narrower spectral width (~3 meV), the lasing photon energy changed sensitively to the excitation photon energy. In the present measurement, the wide spectral width of the excitation (~12 meV) prevents us to observe the variation of the PL photon energy. It is necessary to measure the timeprofiles of the PL spectra by using an excitation laser with narrow spectral width in order to clarify the biexciton transition process and their nonlinearity in CuCl QDs.

4 Summary

We have measured the time-resolved PL spectra of biexciton states in CuCl QDs embedded in NaCl matrices by the optical Kerr-gate method under resonant excitation of the excitons and resonant two-photon excitation of the biexcitons. Under resonant two-photon excitation, the new PL band denoted by FM was observed before the rise of the BM band. The observation of the FM band suggests a new transition process from the biexciton to the exciton state. In addition, the rise times of the M and BM bands,

which were attributed to the free and bound biexcitons, were unexpectedly slow when the biexcitons are generated directly under two-photon excitation, so that we should reconsider the initial biexciton state originating the M and BM bands. The FM band shows a high nonlinearity and has a pulse-shaped time-profile. Furthermore, it is suggested that the FM band is the origin of the laser emission.

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